Chitin Lengthens Power Production in a Sedimentary Microbial Fuel Cell

Chitin in Sedimentary Microbial Fuel Cell

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Abstract— An emerging technology that could be utilized for ocean energy production is the microbial fuel cell. Microbial fuel cells are able to oxidize biodegradable fuels, such as organic waste, to generate electrical power. The sediment microbial fuel cell (SMFC) is a specialized subset of microbial fuel cells relevant in generating energy in the ocean environment.

SMFCs are devices which are able to directly produce electrical energy by bacteria consuming biodegradable compounds in marine sediments. In sediments with low organic carbon, SMFCs have only been observed to provide relatively low amounts of power. Therefore, one hypothesis was to evaluate power production in a SMFC post an addition of an external carbon source. However, because this is in a seawater system, the carbon source should be in a solid phase. Types of solid amendments can include simple plant materials (lignin/cellulose) or animal by-products (chitin, deceased organisms, or other waste products). In this study, chitin from shrimp shell waste was used as a method of increasing organic carbon to increase or prolong power production and for SMFC operation in sandy, low carbon sediments. SMFC's were tested in two San Diego Bay sediment types; low total organic carbon (TOC) and average TOC: 0.2% TOC and 2.5% TOC, respectively. SMFC units with chitin wrapped in water soluble tape were evaluated under static sea water conditions, as well as in the field.

Results for chitin from shrimp shell waste indicated that power density was greater by a factor of 2 relative to control units in sediments with 2.5% TOC; and in sediments with low TOC, 0.2%, power output is 100 times greater. Therefore, these data in both normal and low organic carbon sediments demonstrate that chitin enhances and lengthens power production.

Keywords—chitin; MFC; microbiology; iron-reducing bacteria; sulfate-reducing bacteria; marine

I. INTRODUCTION

Ocean-based energy recovery devices are often based on kinetic or solar energy harvesting. In the marine environment, microbial fuel cells, termed either benthic or sediment microbial fuel cells (SMFC), have been developed to generate power via anodic bacteria in the ocean sediment. These fuel cells capitalize on microbial activity to catalyze these reactions, eliminating the cost and complexity of specialized catalysts used in standard chemical fuel cells [1]. Anodic bacteria in SMFCs transfer electrons to electrodes in the sediment. These electrons are then used to reduce oxygen at the cathode, producing electrical energy. SMFCs can provide an inexpensive means for providing persistent renewable power that can be used to operate low-power sensors or to trickle charge batteries.

In most studies of microbial fuel cells in laboratory settings; an external electron donor is usually added. In laboratory settings, researchers have performed analysis and determined that carbon sources can be provided to manipulate power output [2]. In the preliminary examinations performed by our laboratory, it was observed that in low organic carbon environments, even under flow-through seawater conditions, power production was generally less versus normal organic carbon conditions. Therefore, it was hypothesized that one of the explanations that SMFCs in sandy, low organic sediment underperform may be due to low levels of organic content available as a food source for bacteria in the sediment. Dependent upon applications, there are scenarios where a SMFC would need to function in low-carbon, sandy sediments. Therefore, this research served as a means of adding an inexpensive carbon source to a SMFC in a field environment. In environmental remediation studies, organic content in soils and sediments can be raised by adding inexpensive substrates such as ethanol, molasses, or vegetable oils. In the case of underwater marine sediment, options for carbon amendment are limited to solid carbon amendments to minimize unwanted migration due to diffusion and advection.

In this study, chitin was chosen as a means to amend the SMFC electrodes in marine sediments. One advantage to using chitin is that it is one of the most abundant proteins in the marine system and is also a waste product; therefore, it is cost effective. Another rationale for the incorporation of chitin as an organic carbon source is because it is slow to degrade by bacteria. The author has successfully used chitin before in other studies that demonstrated an increase in bioremediation [3]. Upon degradation, the primary by-products are acetate and a small percentage of lactate (approximately 80% and 5% respectively) [4]. Acetate is an

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environmentally relevant and excellent food source to stimulate primarily iron- reducing bacteria [5] and lactate will stimulate sulfate-reducing bacteria. Both groups of iron-reducing and sulfate-reducing bacteria (FeRB and SRB, respectively) are considered as likely candidates of bacteria to contribute electrons to the MFC anode [6] as both bacterial groups can donate electrons externally.

The chitin was derived from shrimp exoskeleton and was adhered using water soluble tape to graphite plate anodes to feed the indigenous bacterial populations; power production in the SMFC was monitored. The objectives for this study were to determine: (1). if a carbon source, such as chitin could be incorporated into a sedimentary MFC prototype for usage in low carbon environments; (2). if the power produced in low organic carbon environments was equivalent to areas of normal organic carbon; (3). if the chitin would influence the bacteria in the sediment near the anode; and (4). If the primary populations of bacteria present in these samples. Research topic numbers 3 and 4 are still on-going and preliminary results will be provided at the Oceans 2013 Conference.

II. MATERIALS AND METHODS

A. Laboratory Based Experiment

An initial SMFC assembly was set-up in a static system to determine the capability of amending an organic carbon food source to an anode to be used in a SMFC. One gram of organic carbon in the form of practical grade chitin (C7170; Sigma Aldrich; St. Louis, MO, USA) was placed directly on each side of a graphite plate anode (30 cm x 5 cm x 0.3 cm) with water spray, and then polyvinyl alcohol-based water soluble was wrapped around the anode material to keep the organic carbon in place. A titanium wire was secured to the graphite plate to an provide electrical connection to the anode.

Sediment was obtained from the Marine Corps Recruit Depot in San Diego, CA and used to fill an aquarium to a depth of 3-4 inches. Sand-filtered San Diego Bay water was then used to provide overlaying water of about 6 inches. The anodes were embedded in the sediment and the titanium leads were guided out of the tank to a solderless breadboard. Graphite fiber brushes (Mill-Rose Company; Mentor, OH, USA) were used as cathodes and also connected to the breadboard. Passive resistors were then connected between the anode and cathode to provide an external load. The voltage of the anode and cathode were measured (using a Ag/AgCl reference electrode) through a data acquisition system consisting of a a data acquisition unit (Model USB-1616FS; Measurement Computing Corporation; Norton, MA) and a custom data logging program created with Labview (NI Labview 2011; National Instruments Corporation; Austin, TX).

The system was allowed to reach a stable whole cell open circuit potential (around 0.8V) before being loaded with an external load. The systems were checked periodically to maintain a working potential between 0.4 and 0.3 V by changing the resistive load. The systems were operated in the manner until a power production appeared stable over several days.

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B. Field Evaluations

A similar deployment of adding chitin to anodes on a larger scale was performed and deployed in the field. Two grams of chitin was added to each side of a 30 cm x 5 cm x 0.3 cm anode; then the anode was covered with water soluble tape (polyvinyl alcohol) and turned over to cover the other side with 2 g of chitin. Two anodes were placed vertically and parallel to each other exactly 5 cm apart using a wooden box to hold them the anodes in place [7]. The SMFC units containing two electrodes each electrically connected to the fiber-brush cathode were buried at a depth of 20 m of seawater in San Diego Bay with the assistance of US Navy divers. These systems were deployed with a fixed external resistance (200 Ω) based on laboratory results. An additional datalogger (U12-006; Onset Computer Corp; Bourne, MA, USA) was used to monitor the working potential of the field-deployed systems. All the electronics were placed in a waterproofed PVC housing and potted with waterproof epoxy.

Two units were control units; three units were chemically coated with chitosan (a chitin derivative- data not shown) and two units contained the loose chitin around the anode, but wrapped in water soluble tape. The water soluble tape only dissolved one the unit was mostly buried; ensuring that most of the chitin remained in contact with the anode.

C. Microbiology

Microbiological samples for determining differences in bacterial enrichments and for molecular biology were taken on Day 0, Day 3, Day 7, and Day 60. At Day 3, Day 7, and Day 60, the anodes were sacrificed to examine the microbial population directly on the anode. These data are still on-going and will not be shown in this paper; but will be presented at the conference. DNA extraction, PCR-DGGE (denaturant gradient gel electrophoresis) of 16 S ribosomal RNA gene, band excision and sequencing, and phylogenetic analyses followed described protocols in a previous report [3].

III. RESULTS

The laboratory studies examining SMFC power production show an increase in maximum power output when chitin surrounds the anode (Fig. 1). Following a 14 day start up period, the systems exponentially increase power production as an external load is continuously adjusted to bring the operating voltage to a steady state value of 0.4 V (around day 17 for control SMFCs and day 10 for chitin-amended SMFCs). While two of the chitin replicates did not begin significant power production until Day 17, the final steady state power production for those systems were the highest of the systems tested in the field. All six systems appeared to be producing maximum power after day 21, where the external load was 200Ω.

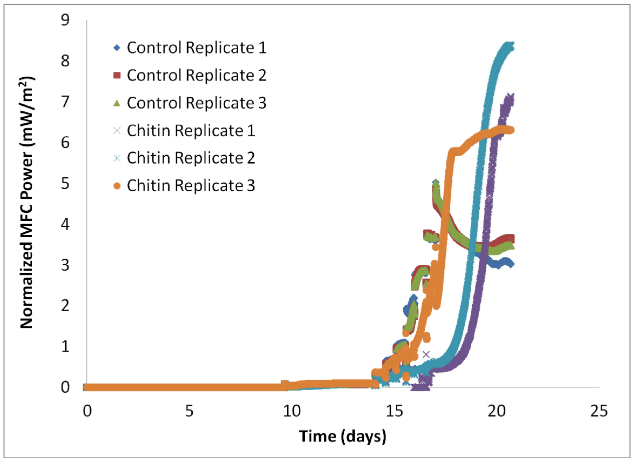

Fig 1. Normalized power output in mW/m^2 in the laboratory experiments in the chitin surrounding the anodes versus control.

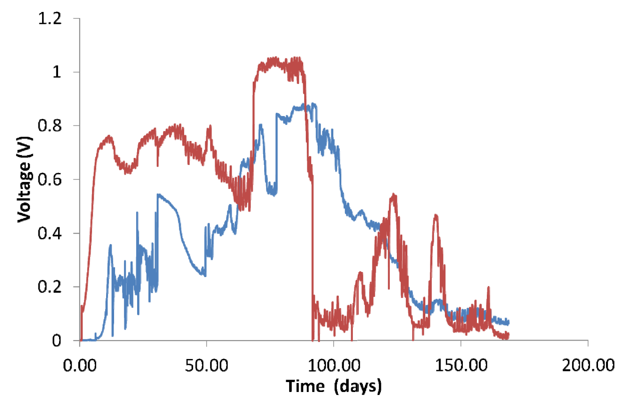

Fig. 3. Voltage output in replicate field SMFC systems deployed with chitin on the anode in field experiments. Power output varies between effectively 3 mW/m^2 and 20 mW/m^2. However, power production seems to be continuous.

For systems deployed in the field, the voltages were fairly variable over the initial 180 days (Figs. 2 and 3). These systems were set at a fixed load of 200Ω based on the previous laboratory studies showing a steady state operation at this load for similar systems. Initial power production was fairly quick compared to laboratory systems, with power production observed within the first few days. The control systems were able to maintain power production for between 20 and 50 days before significant decreases in voltage were observed (signaling SMFC failure). The chitin amended systems were also able to produce power almost immediately, but began showing decreased output after 90-100 days. During this operational period, the cumulative power production (Fig. 5) showed that chitin amendments allowed SMFC systems to increase energy production from 17 W-hrs to 391 W-hrs.

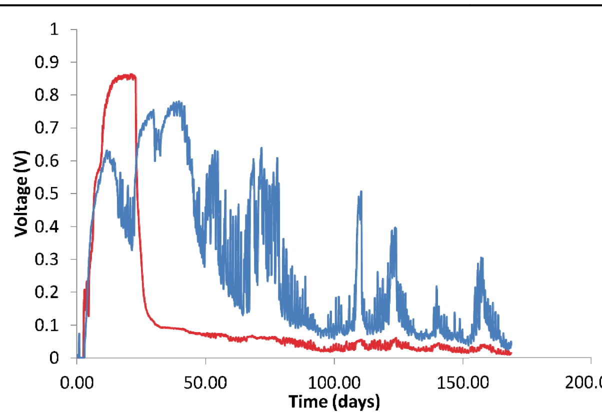

Fig. 2. Voltage in duplicate SMFC control systems (bare graphite) in field experiments. Power output varied between effectively 1 mW/m^2 to peaking at 140 mW/m^2 and then settling at approximately 6 mW/m^2 in the best performer of the controls before dying out at 50 days.

IV. Discussion and Conclusion

The laboratory studies showed similar power development over time. However, some chitin amended systems show a delay in developing power, which could be due to time required to enrich for bacteria necessary to metabolize the chitin. There could also be some effect from the dissolution of the water soluble tape on the bacteria community since dissolution may result in increased alcohol concentration near the anode at the beginning of the experiment.

Figures 3 and 4 show power variability among replicate SMFC systems. This fact is always observed and could be attributed to differences in sediment quality, anode burial, and/or different indigenous bacterial populations. The lack of sustained power output could also be attributed to a lack of sophisticated electronics required to maintain anode potentials at voltages suitable for bacteria enrichment. These systems were only equipped with a passive external resistor and would be unable to adjust SMFC operation for fluctuations in environmental conditions. While the short term operation of these systems showed that chitin can increase overall power production, long term effects are unclear at this point.

Observations made by divers inspecting the systems suggested that burrows around the systems were very prevalent. Burrowing shrimp or worms would adversely affect performance of these systems by introduction oxygen into areas near the anode. The presence of oxygen in these zones would destroy the electrochemical potential gradient that is necessary for these systems to operate. Thus, in future field deployments, care should be taken to prevent marine organisms from interfering with MFC operation. This could be accomplished by physical barriers such as a fine mesh screen or solid plastic sheeting on the sediment surface.

Preliminary DNA analysis of samples from these systems show distinct and different populations exist on chitin amended anodes when compared to unamended SMFC anodes. This would be due to the need for a specific population that is present and able to metabolize chitin and its degradation products. Work is on-going to identify the major

bacteria in the populations and explain the microbial ecology of these systems.

The data presented here give clear evidence to the benefits of amendments for SMFC power production. However, more work is needed to determine long term effectiveness of these amendments. Additional efforts are also needed to understand the impacts of these amendments on the microbiological activity of these systems and if these impacts are ultimately beneficial, harmful, or neutral to SMFC operation and the surrounding environment.

Future planned work involves incorporation of chitin over larger SMFC units to understand whether the enhancement would scale with an increase in system size. More work is also planned on improving energy harvesting efficiency and understanding the impacts of SMFC (both with and without chitin) on the characterization of the benthic microbial population.

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